

## THE INSIDE STORY ON OXYGEN

### A NEW WAY TO LOOK AT THIS ATMOSPHERIC MOLECULE

Oxygen molecules, which make up about 20 percent of the earth's atmosphere, serve as a shield (along with nitrogen, ozone, and other molecules) against ultraviolet radiation from the sun by absorbing the radiation before it reaches the earth's surface.

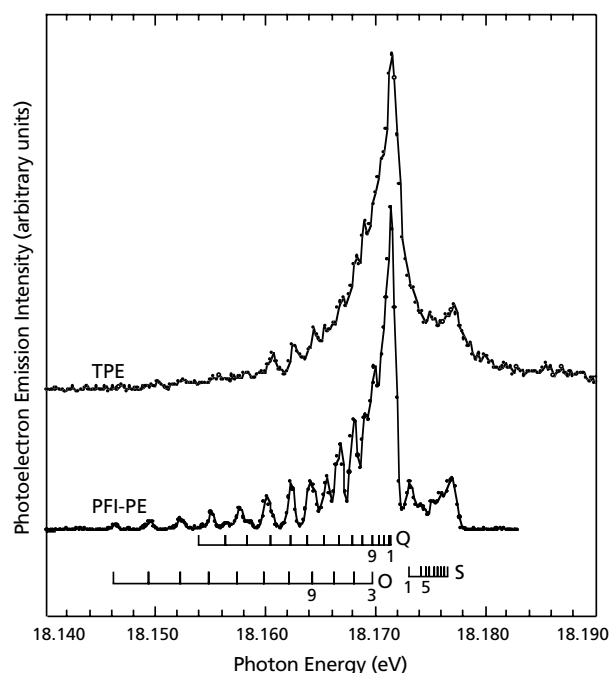
Therefore, understanding the absorption process and the lengthy cycle of subsequent chemical reactions that may lead to the regeneration of oxygen is of deep interest to atmospheric chemists. A key absorption process is photoionization. Upon absorption of a short-wavelength ultraviolet ray (vacuum ultraviolet or VUV) that cannot penetrate through air, an oxygen molecule ejects an electron, thereby becoming a positively charged ion (cation). The ultimate fate of the oxygen depends on the distribution of energy in the cation as the result of photoionization (the internal state of the cation), because this state determines the result when the cation collides with an electron or with another atmospheric molecule.

#### THE ROLE OF SPECTROSCOPY

Understanding the internal state of the oxygen cation ( $O_2^+$ ) comes down to unraveling its electronic structure. In an atom, the outer shell (valence) electrons contribute to the chemical bonding that turns a group of atoms into a molecule. The bonding electrons form orbitals associated with the molecule as a whole rather than the individual constituent atoms. In addition, the atoms in the molecule may vibrate and rotate. Overall, the molecule has a spectrum of energies that depends on the orbitals, with small contributions from the vibrations and smaller ones still from the rotations. This is the electronic structure.

Chemists use VUV spectroscopy to study the electronic structure of molecules. Measuring the wavelengths at which electrons in the molecular

orbitals receive just enough energy to escape but no more (threshold photoelectron spectroscopy) is a sensitive method of probing the molecular electronic structure. Sensitivity is essential, since absorption peaks for molecules that differ only in their rotational motions are very closely spaced and tend to overlap. One big problem is finding a VUV source that provides an intense beam in a narrow wavelength band that can be tuned to the absorption



The advantage of the pulsed-field ionization photoelectron spectroscopy (PFI-PE) technique, as compared to the more conventional threshold photoelectron spectroscopy (TPE), is its ability to resolve spectral peaks due to different rotations in photoionized molecules in excited states. Here the comparison of spectra for molecular oxygen cation ( $O_2^+$ ) shows that the pulsed-field ionization method results in clearly resolved rotational structure that is obscured in the traditional technique. The marks on the Q, S, and O scales indicate where theory says the peaks should be. Comparison of measured spectra with theoretical calculations yields information about the inner workings of the molecule; for example, which electrons and molecular orbitals make dominant contributions to the creation of excited states.

peak of interest. Another is limiting the detection to only the threshold electrons with just enough energy to escape, since electrons in other orbitals that need less energy to escape are also ejected.

### **PUSHING SPECTROSCOPY TO NEW LIMITS**

At the ALS, researchers have successfully attacked these issues by adapting a laser technique to synchrotron radiation. The basic idea is to use VUV light from the ALS to give target electrons almost enough energy to escape, but not quite (exciting them to high- $n$  Rydberg states). A voltage pulse applied a few nanoseconds later then adds the extra energy needed to escape from the Rydberg states, but in the meantime, all the higher-energy electrons have moved out of the area. The researchers call this technique pulsed-field ionization photoelectron spectroscopy.

After an electron escapes from the oxygen molecule, the resulting cation may be left in a variety of internal states with different energies specified by the molecular orbitals and the vibrations and rotations. The ALS provides bright beams of VUV light over a wide range of wavelengths, which scientists can use to probe molecules with electrons in high-energy orbitals (excited electronic states) that are

inaccessible to lasers because of the limited VUV-wavelength range they cover. However, switching light sources creates a new challenge. In the laser version, the time delay between light and voltage pulses is a few microseconds, but light pulses at the ALS come much faster. To meet this challenge, the researchers designed a special photoelectron spectrometer that can reduce the delay to nanosecond intervals.

Researchers have now demonstrated this high-speed, high-resolution capability at the ALS with the molecular oxygen cation. Their results exceed the highest spectral resolving power ever achieved for molecular photoelectron spectroscopy using synchrotron radiation. And the researchers were able, for the first time, to obtain spectra with clearly resolved peaks for the different rotational states of the cation in excited states at energies above those accessible with lasers.

Research conducted by C.Y. Ng (principal investigator), M. Evans, and S. Stimson (Ames Laboratory and Iowa State University); C.-W. Hsu (Berkeley Lab); and P. Heimann (ALS), using the photoionization endstation at Beamline 9.0.2.2. Funding: Office of Basic Energy Sciences of the U.S. Department of Energy.